Extrusion of poly(vinylidene fluoride) filaments: Effect of the processing conditions and conductive inner core on the electroactive phase content and mechanical properties

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Abstract: The phase transformation from the α- to the electroactive β-phase of poly(vinylidene fluoride) (PVDF) extruded filaments submitted to different stretching conditions was investigated. Sample filaments of α-PVDF thermoplastic were extruded and stretched uniaxially at different temperatures (80 ºC to 120 ºC) and stretch ratios (1 to 6). The stretched samples were studied and characterised by x-ray diffraction and quasi-static mechanical experiments. High β-phase contents (~ 80%) are achieved using a stretch ratio of 5 independently of the stretching temperature, between 80 ºC and 120 ºC. Subsequently, in order to obtain filament geometries and material configurations suitable for application, a two layer filament with coaxial layers was produced by coextrusion. The inner layer consisted of a commercially available grade of a conductive thermoplastic with a polypropylene (PP) matrix. For the outer layer the same grade of PVDF was employed. The double-layer filament was also stretched under the same conditions of the PVDF filaments and the results obtained shows that the inner layer material, acting as an electrode, does not have any influence in the PVDF

crystallization process: PVDF crystallizes in the α-phase for stretch ratios of 1 and the α– to β-phase transformation occurs for higher stretch ratios.

Keywords: ferroelectrics; polymers; PVDF; PP; extrusion; mechanical properties; phase transformation.

Introduction

Poly(vinylidene fluoride) (PVDF) is being widely investigated due to its outstanding pyro- and piezoelectric properties among the polymeric materials. These properties are at the origin of various applications, especially in the field of sensor and actuator devices and technologies [1-3]. The existence of these properties is intimately related to the degree of crystallinity, structure and orientation of the crystalline fraction of the polymer, which are, in turn, heavily dependent on the processing conditions [1, 3-12]. Thus optimization studies are important for these materials.

PVDF is a semi-crystalline polymer and is also known for its unusual polymorphism among polymers, presenting at least four crystalline phases, known as α, β, γ and δ [1, 3]. The non-polar α-phase can be readily obtained by crystallization from the melt at high or moderate cooling speeds. If the crystallization occurs at temperatures below 155ºC, the polymer will crystallize in a co-existence of α and γ-phase, and the amount of γ-PVDF present in the sample will increase with the stage time, being be larger for higher crystallization temperatures [1, 3]. The β-PVDF can be obtained by solution if the evaporation of the solvent occurs at temperatures below 70ºC, but the obtained material is porous and shows poor mechanical and electrical properties [12]. The β-phase can be also obtained by stretching the α-PVDF at 80ºC using a stretch ratio (R) between 3 and 5 [11, 12].

The electroactive properties of the material depend on the β-phase content and its micostructural characteristics. Thus, the increment of the β-phase content has always attracted great interest [2, 5-7].

In this work PVDF filaments were extruded in the α and β-phases. In order to determine the influence of the processing conditions in the α to β-phase transformation process, several stretch temperatures and stretch ratios were tested. The amount of each crystalline phase was calculated by X-ray diffraction (XRD). The mechanical properties

of the produced filament were also assessed. In order to prove the suitability of the process for the production of multilayer filaments, combining PVDF with conductive material, PVDF was coextruded with a conductive inner core of a commercially available PP/carbon black thermoplastic composite. The influence of the conductive thermoplastic on the crystalline phase and the α– to β-phase transformation was characterized by XRD and compared to the results obtained for the single PVDF filament.

Experimental

Poly(vinylidene fluoride) (PVDF) supplied from Solvay (Solef Ta-1010) was directly extruded in a prototype monofilament production line under the conditions specified in Table 1

Figure 1 shows the schematic representation of the experimental setup used to produce the PVDF filament. As illustrated, the material leaves the extruder and is cooled in a water bath to reach room temperature. Subsequently, the polymer enters in a system of Rolls 1 that imposes a certain linear velocity. After being heated to a given temperature, in the Heater, the filament is forced to pass through system of Rolls 2, that imposes a higher linear velocity than that of the system of Rolls 1. As a consequence, the filament is stretched in the heater to a stretch ratio (R) given by the ratio of velocities (V) imposed by both systems of rolls: $R = V_{Rolls2}/V_{Rolls1}$..

The water bath after extrusion and the heater are used to ensure that the filament is at a controlled temperature during the latter stretching process and because the filament temperature is more easily controlled during heating than during cooling.

In order to find the optimal processing conditions, several tests were performed, as described in Table 2.

After extrusion, the samples were studied by x-ray diffraction experiments (Siemens D5000) in order to characterise the crystalline phase content. The determination of the β-phase content present in the material was performed by the calculation of the ratio between the area of α– and β-phase crystalline diffraction peaks of the diffractogram. To obtain the areas, peak deconvolution of the diffractograms was performed using Gaussian functions.

Following the production and characterization of the PVDF filaments , a coextruded filament of PVDF with a core of conductive PP/Carbon black composite (PRE-ELEC® PP 1384 from Premix) was produced. The conditions used to obtain the double-layered filament (Figure 2) were equal to the ones of the PVDF filament (see Table 2), using the same prototype monofilament extrusion line but with two single screw extruders, one for each material

Once again, the specimens were characterized by x-ray diffraction (Siemens D5000) in order to study the influence of the conductive core in the crystalline phase content of PVDF.

The mechanical behaviour of the samples was characterized in a universal testing machine from Shimadzu (AG-IS) at room temperature and strain rates $\partial\varepsilon/\partial t$ = 2 mm.min^{-1}.

Results and Discussion

Figure 3 shows the x-ray patterns for PVDF extruded at 80ºC with different stretch ratios. In the diffractogram of the unstretched samples the characteristic diffraction peaks of the α-phase can be observed (Table 3). The broad peak at 2θ = 17.7º corresponds to the (100) diffraction plane and the one at 2θ = 18.4º is related to the (020) planes. A defined diffraction peak at 2θ = 19.9º, identifiable as the diffraction of the (021) plane and another smaller diffraction peak at 2θ = 27.8º corresponding to the (111) diffraction plane are also identified. Other diffraction peaks are observed and identified in Table 3. All these peaks are characteristic of α-PVDF [13] and confirm that the material extruded with R = 1 (unstretched filament) results exclusively in α-phase without traces of β or γ-phases.

The diffractograms of the stretched samples at 80ºC (Figure 3) showed different diffraction patterns. One peak can be observed at 2θ = 20.08º and refers to the sum of the (200) and (110) β-phase diffraction planes and include a residual (110) α-phase plane contribution. A broader feature in the form of a shoulder, which decreases with increasing deformation, can also be observed at 2θ = 18.4º corresponding to the diffractions of (100) and (020) planes of the α-phase. These results indicate that the α to β-phase transformation by stretching at 80ºC is achieved. This process is associated to

the destruction of the spherulitic morphology with polymer chains in a trans-gauche conformation (TCTC$^-$), typical of the α-phase and a formation of a fibrillar structure with an all *trans-planar* zigzag conformation of the β-PVDF [1, 3]. The obtained results are in agreement with recent infrared spectroscopy studies obtained in samples obtained by solvent evaporation, melting and recristalization [11, 12].

In this study, using the baseline method, the amount of β-phase obtained by uniaxial stretch at 80ºC of the PVDF wire was calculated and is presented in Figure 4. It was observed that the β-phase content increases with increasing stretch ratio up to β-phase contents of ~80%, as observed in solution cast films [11, 12].

The baseline method was also applied to the samples processed at 120ºC with different stretch ratios (Figure 4) and it was observed that the phase transformation occurs but the conversion ratio is lower until R = 3, being more pronounced for higher stretch ratios, until it reaches a saturation at ~80% of β-phase for R=5. The amount of electroactive phase achieved in samples stretched at 120ºC is slightly lower than the one obtained at 80ºC. In literature [1, 4, 11, 12], for non-extruded films, it can be found that the optimum processing conditions for temperature and stretch ratios are, respectively, 80ºC and R=5. In this work it was found that by extrusion it is possible to achieve high β-phase content and consequently high α- to β-phase transformation for a stretch ratio of 5 independently of the stretching temperature (from 80 ºC to 120 ºC) at the heater. The observed differences between extruded and non-extruded experiments are explained by the fact that during the non-extruded experimental the material is actually at the stretching temperature during the experiments. On the other hand, during extrusion the material passes through the heater to a gives speed that does not allow the material to reach thermal equilibrium, so the actual stretching temperature of the film is different to the one at the heater.

In order to confirm the effect of the temperature of the heater during stretching, the evolution of the β-phase content for different stretch temperatures at the same permanent stretch ratio (R=5) is reported in Figures 5 and 6. It can be observed that the α- to β-phase transformation slightly decreases for increasing stretching temperatures from 80 to 120 ºC (Figure 6). On the other hand samples stretched at 140ºC are mainly constituted by oriented α-PVDF. This phenomenon is related to the increase in chain mobility due to increasing temperature. At temperatures close to 140 ºC, stretching mainly results in crystal orientation along the stretching direction without considerable

conformational changes. Thus, the resulting material consists predominantly of oriented α-phase [11, 12, 14].

The mechanical properties are among the most important characterization procedures to be performed in polymeric systems, as they will determine the ability of the material to fulfil the final application requirements. Moreover, differences detected among samples may reflect morphological variations that occur due to physical changes on the materials induced by the processing conditions, as it is verified on the stretching stage during the production of the PVDF filament studied in this work. Figure 7 and 8 show the evolution of the *Young* modulus obtained for a sample stretched along the processing (machine) direction.

For samples stretched at 80ºC, the elastic modulus increases almost linearly with stretch ratio and β-phase content. The isotropic structure of α-PVDF is destroyed when a mechanical stress is applied; the polymeric chains and microstructure will get aligned along the direction of the deformation, giving origin to higher Young modulus. The same behaviour was observed in the DMA measurements performed on β-PVDF films [15].

It was observed that the elastic modulus of the samples is almost independent of the stretching temperature at which the samples were obtained (see Figure 8). This fact indicates that the alignment of the microstructure is the key factor that determines the mechanical properties of the filament.

In order to maximize the electroactive response of the β-PVDF polymer it is necessary to apply an electrical poling process to the samples, that consists in applying a high electrical field (some kV of magnitude) [1-3, 16, 17]. The poling field induces a realignment of the crystallite dipolar moments. Before poling, there is a random distribution of the dipolar moments of the individual crystallites. After the poling process there is a biased distribution of the dipoles in space along the direction of the applied electrical field.

In order to achieve the maximum response of the β-PVDF and to be able to use it as sensors and actuators, in film-shaped polymer it is usually necessary to deposit a conductive thin coatings on both surfaces of the polymer. For this purpose, and given the circular shape of the produced filament, in this work a conductive inner filament of PP/carbon black composite was coextruded in the core of the filament (see Figure 2). The results shown in Figures 9 and 10 allow to conclude that the incorporation of the

inner core does not affect the crystalline phase of the PVDF component, and the extruded PVDF crystallizes in α-PVDF for R=1 (Figure 9) and in β–phase for R=5 at 80ºC (Figure 10) as can be observed for the diffraction peaks characteristics of the α and β-phase (Tables 3 and 4, respectively).

The base line was applied to calculate the evolution of the amount of β–crystalline phase present in the coextruded filament stretched at 80ºC with R=5 and the value found is similar to the one obtained for the PVDF wire (80%).

Conclusions

This work has established the fundamentals for the extrusion of PVDF filaments with a core of conductive polymer in order to obtain a piezoelectric filament, capable to be used for sensor and actuator applications.

PVDF polymer was initially extruded at different temperatures and stretch ratios. For the samples stretched at 80ºC, the material presents merely the non-electroactive α-phase for a stretch ratio of 1 and undergoes α to electroactive β-phase transformation, attaining ~ 80% at a stretch ratio of 5. Samples with the same permanent deformation (stretch ratio of 5) have the amount of the electroactive phase between 75 to 80%, for stretch temperatures between 80 to 120ºC. When stretched at temperatures higher than 120ºC, the β-phase content drops to about 22% and the sample mainly shows just oriented α-PVDF.

Quasi-static mechanical measurements reveal that the Young modulus of the wire stretched at 80ºC increase with increasing stretch ratio. For the samples stretched at different temperatures the elastic modulus remains almost constant, indicating that alignment is most important than phase for the mechanical properties of the material.

The PVDF wire with a conductive PP/carbon black composite core crystallizes in the crystalline phase related just to the temperatures and stretch ratio conditions, independently of the existence of the conductive core: for 80ºC the material crystallizes in the α-phase=1 and in the β-PVDF for stretch ratios of 1 and 5, respectively.

Acknowledgements

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Table 1 - Temperature profile employed during extrusion.

Barrel Zone	**Temperature /ºC**
# 1-Feed Zone	160
# 2-Compression Zone	180
# 3-Metering Zone	220
Die	225

Table 2 - Conditions employed during the extrusion experiments.

ID	**Pulling ratio**	**Heater Temperature [ºC]**
Run1	1 to 6	80
Run2	5	90
Run3	5	100
Run4	1 to 6	120
Run5	5	140

Table 3 – Crystalline planes of α-PVDF and the corresponding diffraction angles.

Crystalline planes	**2θ°**
(100)	17.7
(020)	18.4
(021)	19.9
(111)	27.8
(200)	35.7
(002)	39
(022)	57.4

Table 4 – Crystalline planes of β-PVDF and the corresponding diffraction angles.

Crystalline planes	**2θ°**
(200)	20.7
(110)	20.8
(020)	36.6
(101)	36.6
(221)	56.1

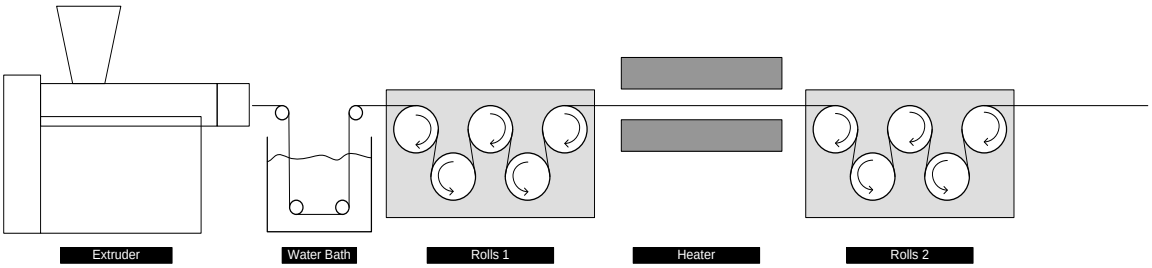

Figure 1 - Monofilament prototype extrusion line used to produce the filaments.

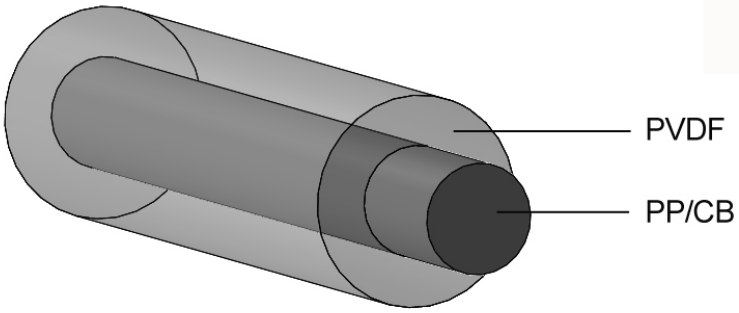

Figure 2 - Double-layered polymeric filament

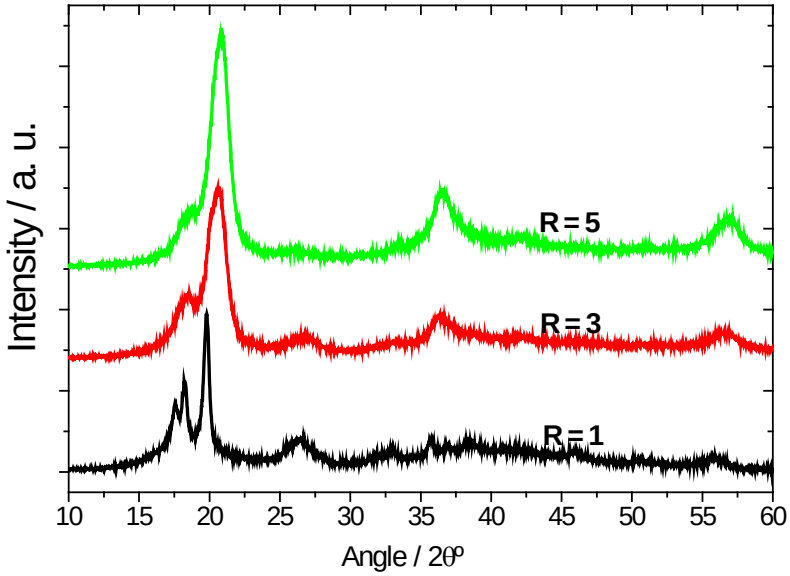

Figure 3 – XRD patterns for the PVDF wire extruded at 80ºC for different permanent deformations.

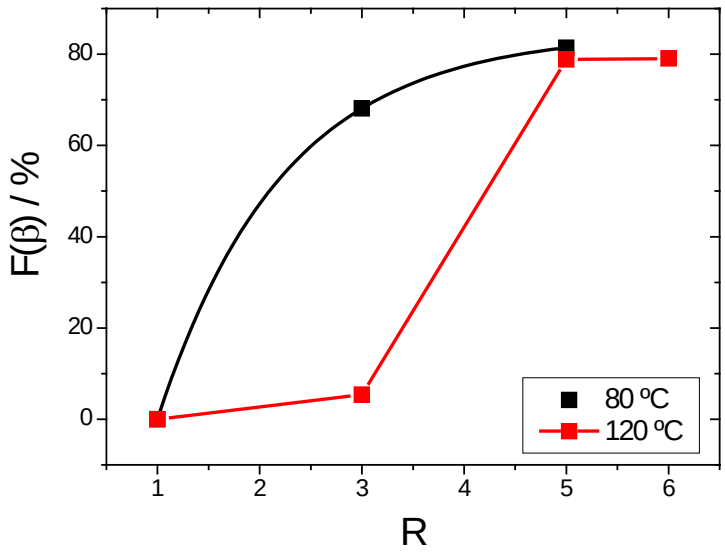

Figure 4 - Amount of β-PVDF for different stretch ratios for the samples processed at 80 ºC and 120 ºC.

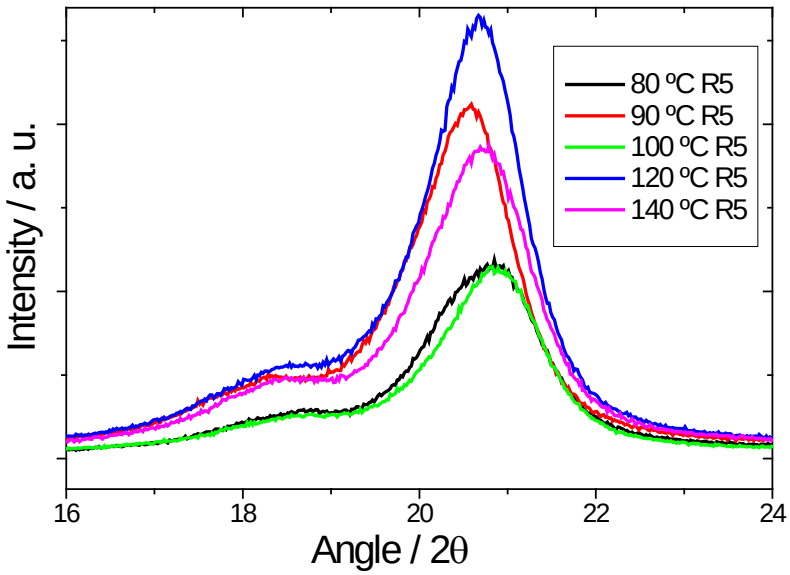

Figure 4- XRD plot for the samples stretched ate different temperatures and with R=5.

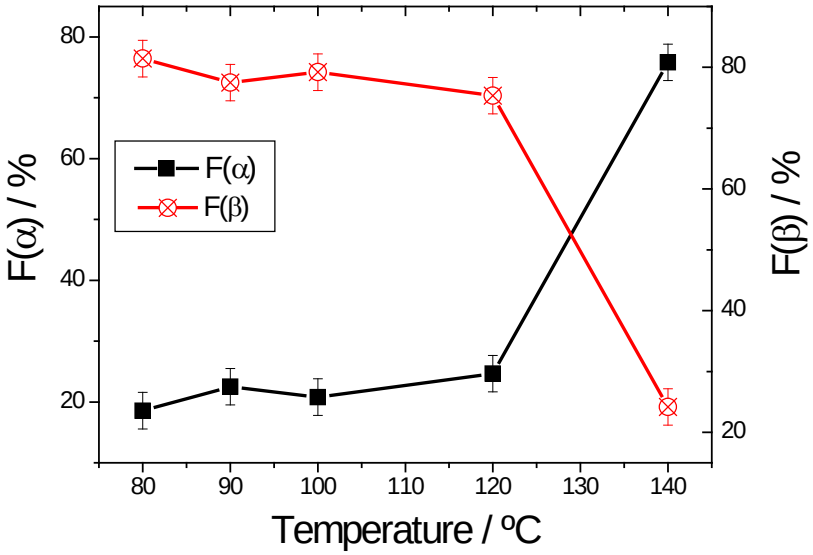

Figure 5- Crystalline phase amount present in the PVDF wire at different processing temperatures and R = 5.

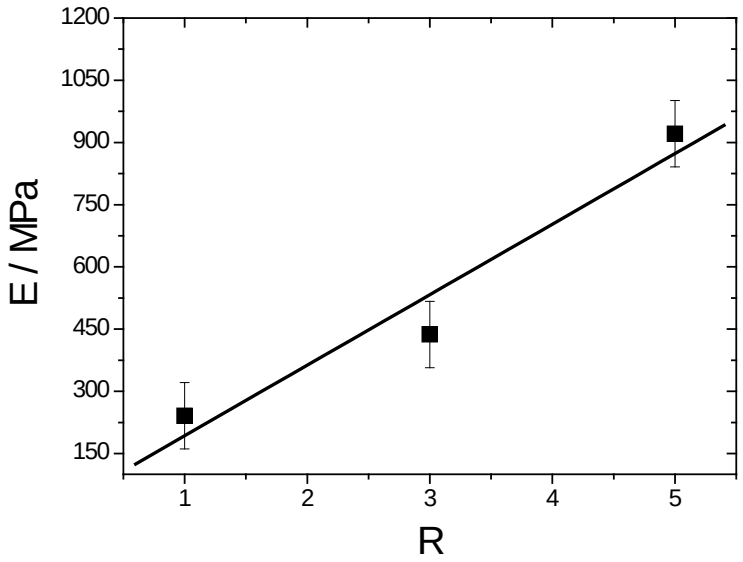

Figure 7- Young Modulus for the samples processed at 80ºC and with various stretch Ratios.

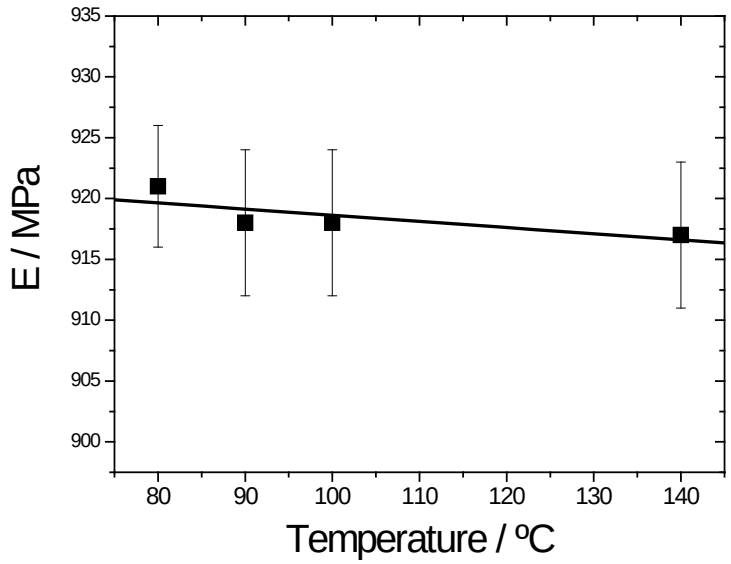

Figure 6- Young Modulus for the samples stretched at different temperatures with R=5.

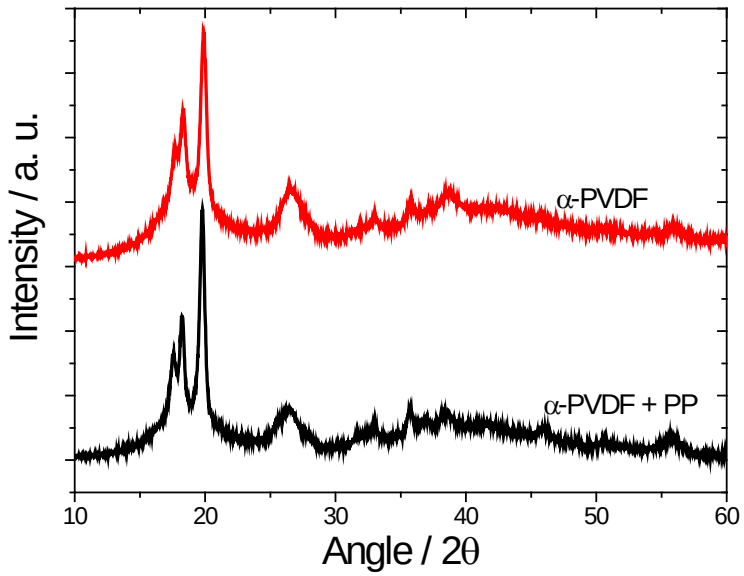

Figure 7- XRD patterns for the α-PVDF wire and for the composite PP Carbon Black/PVDF wire processed at 80ºC and with R=1.

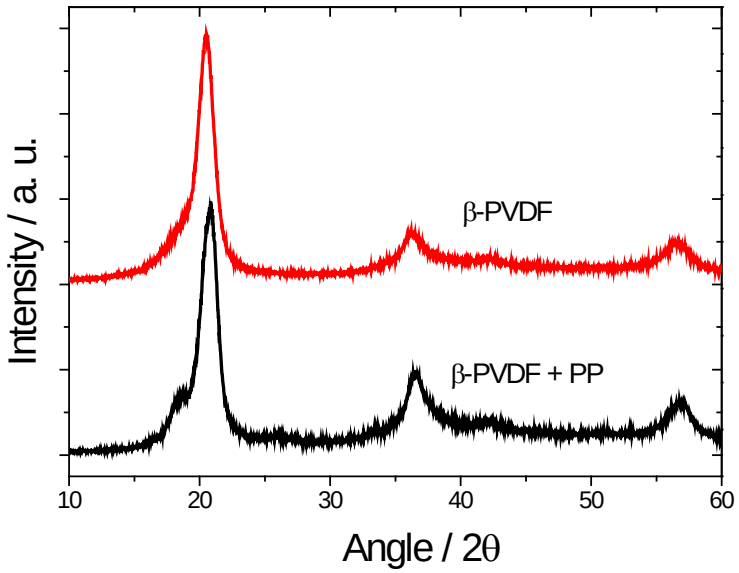

Figure 10- XRD patterns for the β-PVDF wire and for the composite PP Carbon Black/PVDF wire processed at 80ºC and with R=5.